OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1261

R&T Code 4131038

ONR Technical Report ONR Technical Report #30

Discovery of Oriented Gaseous Water Molecules in the Vapor-Liquid Interface of
Water
by

H.C. Allen, E.A. Raymond, M.G. Brown, and G.L. Richmond

Physical Review Letters, submitted

Department of Chemistry
1253 University of Oregon
Eugene, OR 97403

July 2000

20000713 018

DTIC QUALITY INSPECTED 4

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 10 July 2000	3. REPORT TYPE AND DATES COVERED Technical 6/1/99-5/31/00

4. TITLE AND SUBTITLE

Discovery of Oriented Gaseous Water Molecules in the Vapor-Liquid Interface of Water

5. FUNDING NUMBERS

N00014-89-J-1261

6. AUTHOR(S)

H.C. Allen, E.A. Raymond, M.G. Brown, and G.L. Richmond

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Dept. of Chemistry
University of Oregon
Eugene, OR 97403

8. PERFORMING ORGANIZATION REPORT NUMBER

ONR Technical Report #30

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. Peter Schmidt
Office of Naval Research Physical Science and Technology, ONR 331
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY

11. SUPPLEMENTARY NOTES

Physical Review Letters, submitted

12A. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release: distribution unlimited

12B. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Please see attached abstract

14. SUBJECT TERMS

molecular orientation of water molecules

15. NUMBER OF PAGES

15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

Discovery of Oriented Gaseous Water Molecules

in the Vapor-Liquid Interface of Water

H.C. Allen, E.A. Raymond, M.G. Brown, G. L. Richmond

Department of Chemistry

University of Oregon

Abstract

We present the first experimental measurements of the orientation and hydrogen bonding character of interfacial water molecules in their gaseous state in coexistence with the bulk liquid water. These interfacial vapor state molecules are distinct from the surface free OH and the interfacial liquid state water molecules and show a preferred orientation with their hydrogen atoms directed towards the liquid surface.

The goal to develop a molecular level picture of water orientation and bonding at this vapor-liquid boundary where liquid phase water molecules coexist with vapor phase molecules has fascinated scientists for decades. Whereas most theoretical[1-8] and experimental studies[9-11] in recent years are converging on a consistent description of interfacial water on the liquid side of the interface, there is considerable disparity in the theoretical description of water molecules on the vapor side. A primary factor in this lack of consensus is the paucity of available data that unequivocally measures the properties of these interfacial vapor state molecules. As with theoretical efforts in this area, the low density of these vapor state interfacial water molecules is experimentally problematic.

Nevertheless, detection and characterization of these molecules is essential for a complete understanding of interactions at water surfaces. For example, numerous environmental and atmospheric processes rely upon interfacial water to facilitate adsorption and transport.[12,13] It is the interfacial region that is the first to host an adsorbate into the liquid phase. In the atmosphere, water vapor condenses to form a high concentration of submicron sized aerosols that play a central role in air quality,[14] radiation balance[15,16] and the chemistry of atmospheric constituents.[14,17]

In this paper we present the first vibrational spectroscopic measurements of interfacial water vapor species in coexistence with their liquid phase. These detected vapor state molecules have a preferred orientation relative to the surface plane and have minimal hydrogen bonding to adjacent water molecules as manifested in the energy and linewidth of the spectral OH stretching modes examined. These molecules are distinctly different than the water molecules with a dangling bond into the vapor phase,[11] or water in the liquid portion of the interface where hydrogen bonding between water molecules is strong.[9-11]

The technique employed in these measurements is surface vibrational sum frequency spectroscopy (VSFS), a second order nonlinear optical process that is interface specific[18] and has been used in previous studies of the molecular structure of liquid surfaces.[19-22] As a vibrational spectroscopic technique it measures the energy and the intensity of interfacial vibrational modes of water molecules, modes whose energies are highly sensitive to the degree of hydrogen bonding to other water molecules. In addition, due to the coherent nature of sum frequency generation, interferences between vibrational modes provide key information about the relative orientation of interfacial molecules.

Central to the conclusions of this work has been the incorporation of the phase of the SF response in the analysis of the data.[22-25]

The VSF spectra were obtained for water surfaces at an atmospheric pressure of ~1 atm and at ~ 21° C. HPLC grade water or Nanopure water (18 MΩ) was utilized in these studies. The laser system[26] produces 800 nm, 2 ps pulses, 2 mJ of energy, and operates at 1 kHz. The infrared (OPA, 2800 – 3800 cm^{-1}) and 800 nm beams are spatially and temporally overlapped at the interface of interest. The SF beam produced at the interface is collected with a cooled CCD array after spatial filtering. The polarizations of the incident and outgoing SF beams (*p* and *s* polarizations referring to the light polarized parallel and perpendicular to the incident planes, respectively) were selected with appropriate polarization optics. In the experiments described, three different polarization combinations were used, *ssp*, *sps*, and *ppp* where the three indices for the different combinations refer to the polarization of the SF response, the 800 nm and the infrared beams, respectively. The *ssp* polarization combination probes the macroscopic 2nd order susceptibility element, $\chi^{(2)}_{yyz}$, which contains information on the resonant IR transition moments perpendicular to the surface and the isotropic resonant Raman response. The *sps* polarization combination probes the $\chi^{(2)}_{yzy}$ element, which gives information on the resonant IR transition moments parallel to the surface and the anisotropic resonant Raman response. The *ppp* combination probes the $\chi^{(2)}_{zzz}$, $\chi^{(2)}_{xxz}$, $\chi^{(2)}_{xzx}$, and $\chi^{(2)}_{zxx}$ elements.

Critical to the discovery of these vapor phase water molecules from the VSF spectrum has been the development and application of a more rigorous spectral analysis for water than has been used previously in VSF studies of the air/water interface. This

analysis[23] takes into account the symmetry of the vibrational modes of water, the relative phase of these vibrational modes, and the polarization of incident and outgoing fields. The $\chi^{(2)}_{ijk}$ components discussed above are the measured macroscopic quantities arising from the individual molecular hyperpolarizabilities described by β. The symmetry of the water species and its contributing OH stretching vibrational modes are used to reduce the 27 element molecular hyperpolarizability tensor β to its nonzero elements. The set of nonzero β elements are then transformed from the molecular axes to the laboratory axes. This is completed utilizing the Euler angle transformation matrix, $\mu_{ijk:lmn}$, thus changing the molecular axis system with coordinates a, b, and c, to the laboratory axis system i, j, and k. The Euler angles are described by χ, ϕ, and θ, where χ is the rotation about the highest symmetry axis, ϕ is the orientation around the surface normal, and θ is the orientation of the symmetry axis relative to the surface normal. We assume an isotropic distribution for χ. The observed 2nd order macroscopic susceptibility component $\chi^{(2)}_{ijk}$ (not related to the Euler angle χ),

$$\chi^{(2)}_{ijk,v} = \sum_{lmn=abc} \mu_{ijk:lmn}\, \beta_{lmn,v}\,, \tag{1}$$

for each vibrational mode is the sum of the Euler angle transformations of the contributing β elements. The macroscopic susceptibility, $\chi^{(2)}_{ijk,v}$, is the macroscopic property probed in these experiments. When vibrational modes of overlapping energies exist, the resulting SF responses from these modes can interfere. For the symmetric stretch, v_1 (A1 symmetry) for a water molecule, equation (1) leads to the following result for *ssp* polarizations,

$$I(ssp)_{SF(C2V, A1)} \propto |\chi^{(2)}_{yyz,nr} + \mu_{yyz:aab}\,\beta_{aab,v1} + \mu_{yyz:bbb}\,\beta_{bbb,v1} + \mu_{yyz:ccb}\,\beta_{ccb,v1}|^2\,I_{IR}\,I_{vis}\,, \quad (2)$$

where $I(ssp)_{SF(C2V,A1)}$ is the measured sum frequency intensity and $\chi^{(2)}_{nr}$ is the nonresonant $\chi^{(2)}$, which for this system is small. The axis of highest symmetry is the b axis, and the water molecule lies in the ab plane. The I_{IR} and I_{vis} are the intensities of the incident beams that mix to produce the SF photons. For the asymmetric stretch of water, v_3 (B2 symmetry),[27] the sum frequency intensity has the form,

$$I(ssp)_{SF(C2V, B2)} \propto |\chi^{(2)}_{yyz,nr} + \mu_{yyz:aba}\,\beta_{aba,v3} + \mu_{yyz:baa}\,\beta_{baa,v3}|^2\,I_{IR}\,I_{vis}\,. \quad (3)$$

The cross terms in equations (2) and (3) lead to the observed interference effects.[22-25]

Figure 1 shows the *ssp* spectrum of the vapor-liquid interface of water. The *sps* and *ppp* VSF spectra are shown as an inset in the figure. The spectral region explored in this study corresponds to the OH stretching modes of interfacial water. At lower energies (3000– 3500 cm^{-1}), the SF spectrum of interfacial water is dominated by broad spectral features that correspond to cooperative motions of tetrahedrally hydrogen bonded water molecules. Spectral features at higher energies, the focus of this study, correspond to loosely associated water molecules. Figure 2 focuses on this portion of the spectrum. Previous studies have assigned the intense peak at ~3702 cm^{-1} in the *ssp* (and *ppp*) spectra to the stretch of the OH dangling bond, or free OH.[11] The free OH peak encompasses modes of both 3-coordinate and 2-coordinate OH dangling bond species.[28] Its energy is also coincident with the uncoupled OH of gas phase HOD molecules.[29]

The improved quality of our data in this free OH region over previous studies coupled with the more comprehensive analysis brings to light new features that provide evidence for the presence of vapor state molecules in the interfacial region. The most obvious feature in the *ssp* spectrum that supports this claim is the small but distinct spectral peak observed at ~3770 cm^{-1} (peak fit to 3763 cm^{-1}) that we assign to the asymmetric stretch (AS) of the interfacial vapor state water species. The AS and the symmetric stretch (SS) of gas phase water monomers are observed at 3756 cm^{-1} and 3657 cm^{-1}, respectively. From the peak positions and the narrow spectral width, we conclude that these water molecules do not hydrogen bond as proton donors to other water molecules. Such an interaction would shift the monomer AS and SS modes to longer wavelengths as seen in other studies.[30] The AS of water vapor molecules oriented with their two hydrogen atoms pointing towards the liquid would be expected by the above analysis to constructively interfere (in-phase) with the free OH SF response observed at 3702 cm^{-1} (fit to 3710 cm^{-1}). This is exactly what is observed. For interfacial vapor state molecules with this orientation, the SF response from the related SS mode and the free OH stretch destructively interfere (out of phase). The presence of both the SS and AS modes are confirmed in our spectra by employing the spectral fitting procedure described above that takes into account the relative phase relationships between these modes and the free OH mode. The fit to this region of the spectrum is shown in Figure 2(a). In Figure 2(b), the three peaks, convolutions of Gaussian and Lorentzian functions, and their relative phases (represented by their signs) that contribute to the spectral fit are shown. In order for the calculated spectrum to accurately fit the experimental data, the orientation of the symmetry axis of the vapor state water molecule must be constrained to $90° < \theta <$

6

180° relative to the surface normal. Attempts to change this constraint resulted in a significantly inferior fit to the spectrum. We therefore conclude that the angle of the vapor state water species is oriented with its hydrogens toward the bulk liquid.

The clear contribution in the spectra from the SS and AS of the vapor water molecules demonstrates our sensitivity to measurement of these low density vapor species in the interfacial region. The resultant interference information from the spectral fits provides the orientation of the interfacial vapor molecules relative to the free OH. The full fit is shown in Figure 1, which assumes broad peaks in the $3000 - 3500$ cm^{-1} region corresponding to the previously assigned collective modes of hydrogen bonded water molecules.[20]

Important to this analysis is the angular orientation of the free OH that protrudes into the vapor. Accurate determination of the free OH angle requires a measurable SF signal in this region under both *ssp* and *sps* polarization combinations. We have obtained the *sps* spectrum of the air-water interface (Figure 1 inset) corresponding to the in-plane and Raman anisotropic response, which has not been previously achieved. Although the spectrum is somewhat featureless, there is measurable VSF signal. We calculate the angle of the free OH to be $28° \pm 13°$ from the surface normal, improving significantly on the previous angle measurements by Shen et al.[11] The weak but measurable signal in the $3100 - 3500$ cm^{-1} region provides evidence for hydrogen bonded water molecules at the interface that have contributions to their dipole moments in the plane of the interface.

There have been a number of theoretical investigations of the vapor-liquid interface of water to which this work can be compared. These studies have largely interpreted the vapor state interfacial region as being comprised primarily of water

molecules containing the free OH bond. We show here that the interfacial vapor state molecules are a separate species from the free OH and their existence and orientation must be included in a full description of the interfacial region. The theoretical deficiency in describing the vapor state of this interface has been recognized in the literature [1] and has been attributed to the limitation of the number of water molecules used in the calculations and the intrinsically lower density of the interfacial vapor region. The collective orientation of the vapor state molecules is likely caused by electrostatic interactions with the liquid phase. On the liquid side of the interface where surface water molecules display stronger hydrogen bonding, we show evidence that there are water species in the interfacial liquid region that have dipole contributions in the surface plane (Fig. 1 inset, *sps*), consistent with several theoretical predictions.[1-8,31] The fits to the *ssp* data and the strong signal in the $3000 - 3500$ cm^{-1} region of the spectrum (Figure 1) also suggest a significant fraction of the liquid state hydrogen bonded water molecules have a component of their dipole moment perpendicular to the interfacial plane, consistent with previous SHG and VSFS experiments.[9-11] Interestingly, we have also found that the vapor state orientation is quite stable in that attempts to modify the interfacial vapor state water orientation by changes in the composition (e.g. pH, salt, ionic surfactants) of the aqueous phase were unsuccessful. No spectral changes in this region were observed although changes were observed in the hydrogen bonded liquid spectral region. Further studies of this spectral region will appear in a later publication. Preliminary studies with moderate temperature changes (15°-25° C) also had a negligible effect on the spectra in the region of Figure 2.

The experiments described herein provide the most detailed picture of the vapor-liquid interface that has been measured to date (Figure 3). In particular, the studies are the first measurement of the structure and orientation of relatively isolated water molecules that exist in the vapor region directly above the liquid surface. These vapor state water molecules are aligned by the interfacial electric field created by the boundary. VSF polarization studies including both the out-of-plane (*ssp*) and the small in-plane (*sps*) SF responses confirm this (see Fig. 1), yet it is the phase information (Fig 2b) that provides the directional information for the vapor state orientation with its hydrogens pointing towards the liquid surface, i.e. opposing the free OH. The findings presented here will further contribute to the understanding of interfacial transport, that is adsorption and accommodation by aqueous solution surfaces. Yet, the implications of this work go beyond the understanding of simple interfacial adsorption, they bring a new level of understanding to the processes and the mechanisms of adsorption and transport.

References

[1]M. A. Wilson, A. Pohorille, and L. R. Pratt, J. Phys. Chem. **91**, 4873 (1987).

[2]M. A. Wilson, A. Pohorille, and L. R. Pratt, J. Chem. Phys. **88** (5), 3281 (1988).

[3]F. H. Stillinger and A. Ben-Naim, J. Chem. Phys. **47** (11), 4431 (1967).

[4]V. P. Sokhan and D. J. Tildesley, Mol. Phys. **92** (4), 625 (1997).

[5]M. Matsumoto and Y. Kataoka, J. Chem. Phys. **88** (5), 3233 (1988).

[6]R. S. Taylor, L. X. Dang, and B. C. Garrett, J. Phys. Chem. **100**, 11720 (1996).

[7]K. A. Motakabbir and M. L. Berkowitz, Chem. Phys. Lett. **176** (1), 61 (1991).

[8]B. Yang, D. E. Sullivan, and C. G. Gray, J. Phys.: Condens. Matter **6**, 4823 (1994).

[9]M. C. Goh, J. M. Hicks, K. Kemnitz, G. R. Pinto, K. Bhattacharyya, K. B. Eisenthal, and T. F. Heinz, J. Phys. Chem. **92** (18), 5074 (1988).

[10]K. B. Eisenthal, Acc. Chem. Res. **26**, 636 (1993).

[11]Q. Du, R. Superfine, E. Freysz, and Y. R. Shen, Phys. Rev. Lett. **70** (15), 2313 (1993).

[12]W. J. De Bruyn, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, J. Geophys. Res. **99** (D8), 16 (1994).

[13]D. J. Donaldson, J. Phys. Chem. A **103**, 62 (1999).

[14]B. J. Finlayson-Pitts and J. N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere*, 1 ed. (Academic Press, 2000).

[15]S. E. Schwartz and M. O. Andreae, Science **272**, 1121 (1996).

[16]S. E. Schwartz, Pure and Applied Chemistry **66**, 178 (1994).

[17]A. D. Clarke, D. Davis, V. N. Kapustin, F. Eisele, G. Chen, I. Paluch, D. Lenschow, A. R. Bandy, D. Thornton, K. Moore, L. Mauldin, D. Tanner, M. Litchy, M. A. Carroll, J. Collins, and G. Albercook, Science **282** (5386), 89 (1998).

[18]C. D. Bain, J. Chem. Soc. Faraday Trans. **91**, 1281 (1995).

[19]Y. R. Shen, Surface Science **299/300**, 551 (1994).

[20]D. E. Gragson, B. M. McCarty, and G. L. Richmond, J. Phys. Chem. **100** (34), 14272 (1996).

[21]S. R. Goates, D. A. Schofield, and C. D. Bain, Langmuir **15**, 1400 (1999).

[22]K. Wolfrum and A. Laubereau, Chem. Phys. Lett. **228**, 83 (1994).

[23]M. G. Brown, E. A. Raymond, and G. L. Richmond, (in preparation) (2000).

[24]C. Hirose, N. Akamatsu, and K. Domen, Applied Spectroscopy **46** (6), 1051 (1992).

[25]J. Lobau and K. Wolfrum, J. Opt. Soc. Am. B **14** (10), 2505 (1997).

[26]D. E. Gragson, B. M. McCarty, and G. L. Richmond, J. Opt. Soc. Am. B **13** (9), 2075 (1996).

[27]P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic Press, New York, 1979).

[28]V. Buch and J. P. Devlin, J. Chem. Phys. **94** (5), 4091 (1991).

[29]J. R. Scherer, "Chapter 3. The vibrational spectroscopy of water," in *Advances in Infrared and Raman Spectroscopy*, edited by R. J. H. Clark and R. E. Hester (Heyden, Philadelphia, 1978), Vol. 5, pp. 149.

[30]L. F. Scatena and G. L. Richmond, (submitted) (1999).

[31]R. M. Townsend and S. A. Rice, J. Chem. Phys. **94** (3), 2207 (1991).

Figure Captions

Fig. 1. VSF *ssp* spectrum of the vapor-liquid interface of water in the OH stretch region. The smoothed curve is the calculated fit that takes into account the phase of the nonlinear response from the symmetry of the modes and the orientation of the molecular axes. The inset shows the VSF *ppp* spectrum (-) and the *sps* (▬) spectrum of the same interface.

The *sps* spectrum reveals significant SF intensity ($3100 - 3500$ cm^{-1}) from the component of the interfacial water bisectors that lay in the plane of the interface.

Fig. 2. (a) The VSF spectrum of the free OH region. The small peak at higher energy is assigned to the asymmetric stretch (AS) of gas phase water. The curve fit is shown. (b) The 3 peaks and their signs (phase of the SF) reveal the existence of the symmetric stretch (SS) of vapor state water molecules. The VSF response from the SS is out of phase with the free OH (and the AS). Thus, the vapor state water molecules are oriented with their hydrogens pointing toward the liquid.

Fig. 3. Preferential orientations of water molecules within the vapor-liquid boundary region is illustrated. The illustration shows, from top to bottom, the oriented interfacial vapor state molecules ($90° < \theta < 180°$), the free OH ($28° \pm 13°$), and the interfacial liquid state molecules.
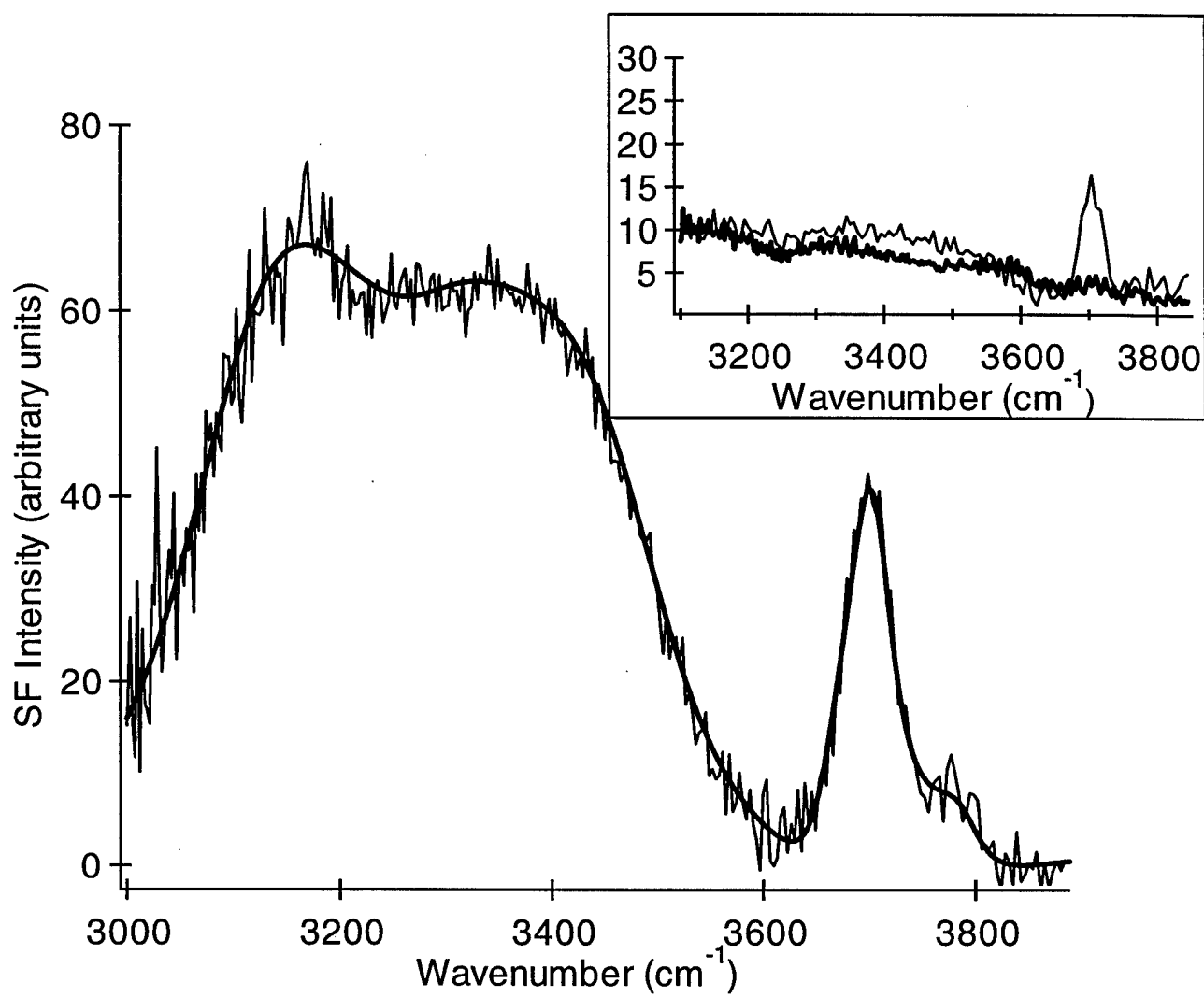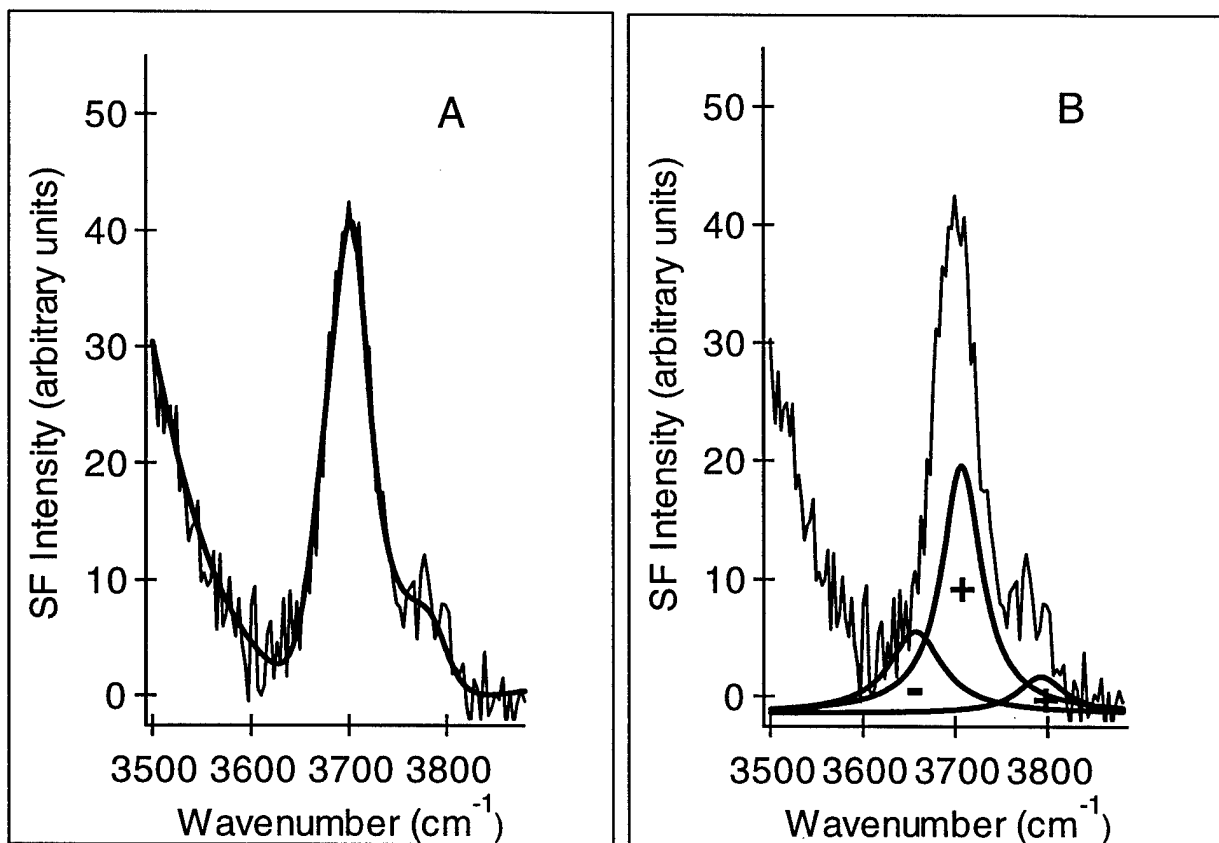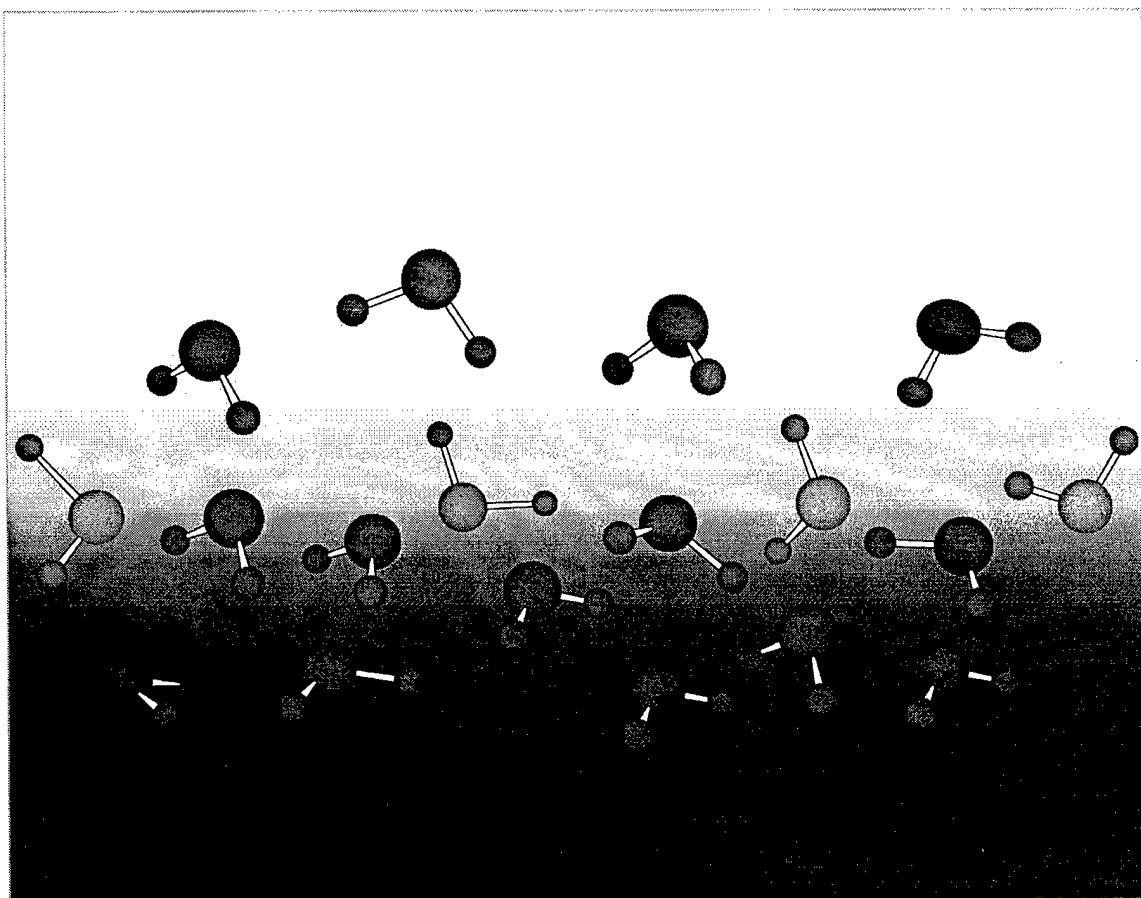
Fig. 1

Fig. 2

Fig. 3